Aluminum Infiltration into Molybdenum Silicide Preforms

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The presence of Mo_5Si_3 in $MoSi_2$ preforms hinders the reactive infiltration of aluminum. To understand the role of Mo_5Si_3, the kinetics of aluminum infiltration into pure Mo_5Si_3 is studied. Irrespective of the initial composition ($MoSi_2$ or Mo_5Si_3) of the preform, the final product always contains $Mo(Al,Si)_2$. However, the aluminum content in the two cases is different: when the preform is $MoSi_2$, the aluminum content is 14-18 at.%, and, when the preform is Mo_5Si_3, the aluminum content is 25-27 **at.%. The activation energy for the reactive infiltration of aluminum into the Mo_5Si_3 preform is ~26 kJ/mol.**

I. Introduction

REACTIVE MELT INFILTRATION (RMI) is a versatile method for preparing ceramic–metal composites. Here, a molten metal wets the surface and reacts with the preform while penetrating into it. This type of wetting-assisted infiltration, without the application of external pressure, provides near-net-shaped products with less residual porosity and has the potential to form a metal–ceramic composite with controlled composition and properties. Reactive infiltration of aluminum into $MoSi_2$ is one such example.[1] Here aluminum reacts with $MoSi_2$ to form a $Mo(Al,Si)_2$ and Al–Si composite as follows:

$$MoSi_2 + 2xAl \rightarrow Mo(Al_xSi_{1-x})_2 + 2xSi \quad (1)$$

This chemical reaction enhances wetting and, hence, infiltration. A capillary rise/viscous flow mechanism and chemical reaction[2–4] may explain the infiltration rate. For example, an activation energy of 8.4 kJ/mol has been found for the infiltration of lead into a copper powder compact.[3] This value is very close to the activation energies for viscous flow and self-diffusion of liquid lead. Where the infiltration process is governed by a chemical reaction, activation energy values are very large, as in the infiltration of aluminum into $MoSi_2$, which is ~300 kJ/mol.[1]

$MoSi_2$ is a potential structural material for use in aggressive environments. It has been reported that the addition of aluminum and formation of $Mo(Al,Si)_2$ improves the mechanical and oxidation properties of $MoSi_2$.[5,6] Infiltration may be one of the processes to obtain a composite of aluminum and $Mo(Al,Si)_2$. Irrespective of infiltration conditions, 14–18 at.% of aluminum has been found to react with $MoSi_2$.[1] To absorb the byproduct silicon, a preform of a mixture of elemental molybdenum and $MoSi_2$ is used, and the final composition after infiltration contains no free silicon.[7]

In an attempt to decrease the aluminum content in the final composite, a $MoSi_2$–Mo mixture was hot-pressed at 1500°C to obtain an 85% dense preform. After the preform was sintered, it was found to contain $MoSi_2$ and Mo_5Si_3. The infiltration rate was not as high as that in pure MoSU. The presence of Mo_5Si_3 impurities may have affected the rate of infiltration. To test this hypothesis, we conducted RMI into pure Mo_5Si_3 preforms, and we present the results in this communication.

II. Experimental Procedure

$MoSi_2$ (2.93 μm, Japan New Metals, Osaka, Japan) and 23.37 wt% molybdenum (3.8 μm, Aldrich Chemical Co., Milwaukee, WI) were mixed and hot-pressed at 1700°C and 22 MPa pressure in an argon atmosphere to form Mo_5Si_3. The infiltration was conducted by placing a solid Al-Si (12.2 wt%) alloy on top of the $MoSi_2$–Mo compact. Infiltration was first conducted at 1200°C for 15 min and then increased to 1600°C, where it was held for 10 min. After infiltration, the sample was cut and the cross section was polished with 1 μm diamond paste to determine the microstructure and extent of infiltration,

To synthesize Mo_5Si_3 compacts, molybdenum and silicon (6 μm, Aldrich Chemical Co.) powders were mixed in stoichiometric proportion, and the mixture was hot-pressed in a graphite die at 1600°C and 16 MPa. An 80% dense Mo_5Si_3 was obtained, which then was cut in equal-sized (4.8 mm X 3,5 mm X 3.5 nun) rectangular bars. Infiltration was conducted by placing the solid Al-Si pieces over the preform bars, inside a graphite crucible. The infiltration temperature was varied 1200°–1500°C, keeping the duration constant at 20 min. For the other set of experiments, the duration of infiltration was 20-60 min, keeping the temperature constant at 1400°C. Infiltrated samples were cut and each cross section was polished to study the infiltration process.

X-ray diffractometry (XRD; Model D/MAX 2200 Ultima, Riguku, Tokyo, Japan) and scanning electron microscopy (SEM; Model 440, Leo Electron Microscopy, Ltd., Cambridge, U.K.) were used for characterization studies.

HI. Results and Discussion

The XRD pattern (Fig. 1(a)) of a sintered $MoSi_2$ -I- Mo sample shows the presence of $MoSi_2$ and Mo_5Si_3. After infiltration with aluminum alloy (Fig. 1(b)), the sample contained only $Mo(Al,Si)_2$ and the aluminum alloy. In a 2.5 mm thick sample, infiltration was not complete, even though the infiltration was first conducted at 1200°C for 15 min, then held at 1600°C for 10 min. In an 85% dense $MoSi_2$ preform of the same thickness, the infiltration was complete in 20 min at 1200°C.[1] Therefore, irrespective of initial composition, the final product was always $Mo(Al,Si)_2$. However, the rate of infiltration depended on the composition of the preform. In this case, the rate may have decreased because of the presence of Mo_5Si_3 in the initial preform.

The microstructure of the infiltrated Mo_5Si_3 at 1400°C for 20 min is shown in Fig. 2. The infiltrated zone, uninfiltrated zone, and the interface zone between them are shown. The black region is aluminum alloy and the dark-gray region contains aluminum (~74 at.%), molybdenum (-21 at.%), and silicon. The dark-gray phase is mainly present in the interface region. Light-gray hexagonal particles are $Mo(Al,Si)_2$. On average, 25-27 at.% of the aluminum is present in these $Mo(Al,Si)_2$ grains, whereas 14–18 at.% aluminum is present in the $Mo(Al,Si)_2$ grains after the infiltration of the

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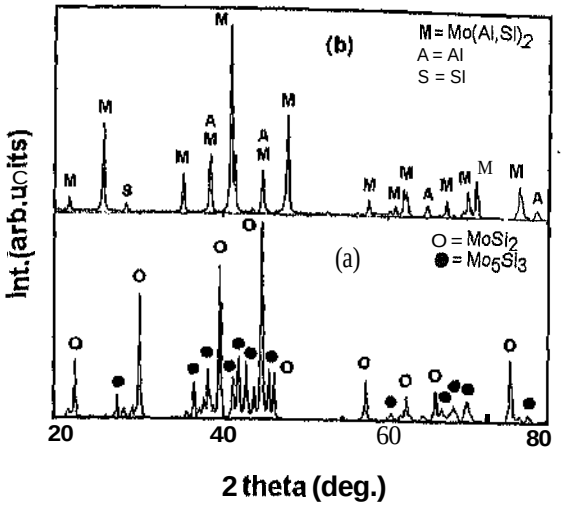
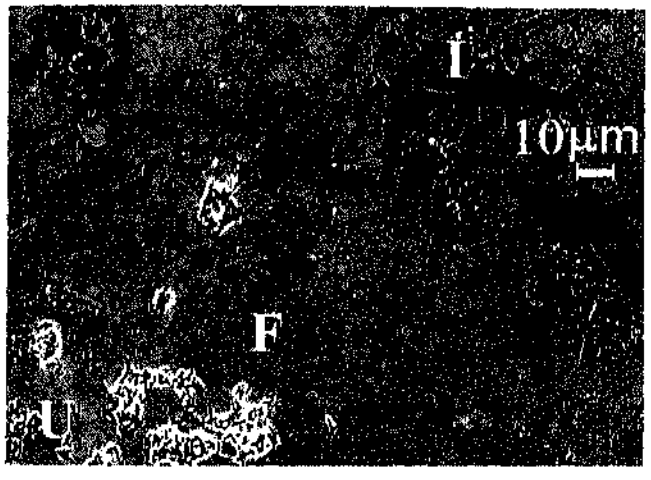


Fig. 1. XRD pattern of sintered $MoSi_2$ + Mo sample (a) before and (b) after aluminum infiltration.



MR. 2. SUM of infiltrated Mo_5Si_3 at 1400°C for 20 min, showing the (I) infiltrated, (U) uninfiltrated, and (F) interface zones.

$MoSi_2$ preform. The composition of the $Mo(Al,Si)_2$ formed after the infiltration depends on the chemical composilion of the preform. Well developed hexagonal grains are found throughout the infiltrated zone, except near the infiltration front. The microstructure of the infiltrated composite depends on the initial perform, When Ihe preform is Mo_5Si_3, hexagonal grains occur after infiltration at 1200°C, but when the preform is $MoSi_2$ + Mo, hexagonal grains are formed only on sintering the sample at 1600°C after infiltration at 1200°C. This may he because of the higher aluminum content in the $Mo(Al,Si)_2$ grains formed after infiltration into Mo_5Si_3 prd'orm, Mo_5Si_3 samples infiltrated at 1400°C and for u longer time (~30 min) show well-developed hexagonal crystallike structures of $Mo(Al,Si)_2$ (Fig. 3), The chemical composilion of these structures is the same as that of the light-gray hexagonal particles shown in Fig. 2.

X-ray mapping of the infiltrated Mo_5Si_3 sample is shown in Fig. 4. Molybdenum and aluminum are well distributed and dense in the interface zone, as compared with the infiltrated zone, where grains are well developed. Molybdenum that is coming out after the reaction of aluminum with Mo_5Si_3 forms a different phase with iiluminum that is present mainly in the interface region. Hence, in this region, iiluminum and molybdenum arc present over Ihe entire area, whereas, in the infiltrated zone, there are places where iiluminum and molybdenum do not coexist. Mo_5Si_3 reacts with aluminum as follows:

$$Mo_5Si_3 + 2xAl \rightarrow Mo(Al_xSi_{1-x})_2 + 4Mo + (1-2x)Si \quad (2)$$

Fig. 3. SEM of the fractured surface of Mo_5Si_3 infiltrated at 1400°C for 30 min. Well-developed hexagonal crystallike structures of $Mo(Al,Si)_2$ are shown.

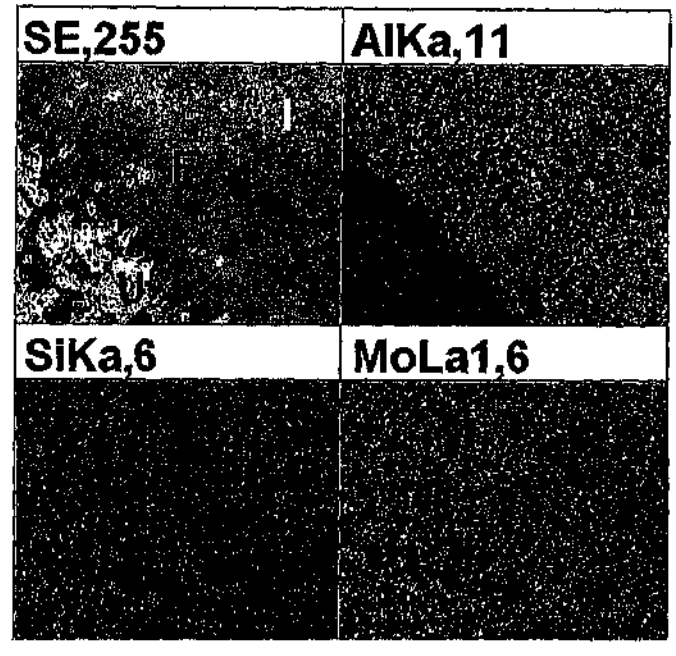


Fig. 4. X-ray mapping of infiltrated Mo_5Si_3 at 1400°C for 20 min, showing the infiltration front ((I) infiltrated, (U) uninfiltrated, and (F) interface zones).

The elemental molybdenum that is released after the reaction diffuses in a direction opposite to the infiltration direction. This molybdenum reacts with the aluminum to form a dark-gray Mo-Al alloy phase.

The activation energy for the infiltration of aluminum into Mo_5Si_3 is calculated using the Arrhenius equation in the following form (where the reaction rate constant, $K = CL/t$, where C is the proportionality constant):

$$\frac{CL}{t} = A \exp\left(\frac{-E_a}{RT}\right) \quad (3)$$

where A is the Arrhenius constant, L the infiltration length, t the infiltration duration, T the infiltration temperature, and R the universal gas constant. / was maintained at 20 min in the first set of experiments. The logarithm of infiltration length as a function of inverse temperature is shown in Fig. 5(a). The slope of the plot gives the activation energy (E_a) of the process, which is ~26 kJ/mol. In the next set of experiments, temperature was maintained

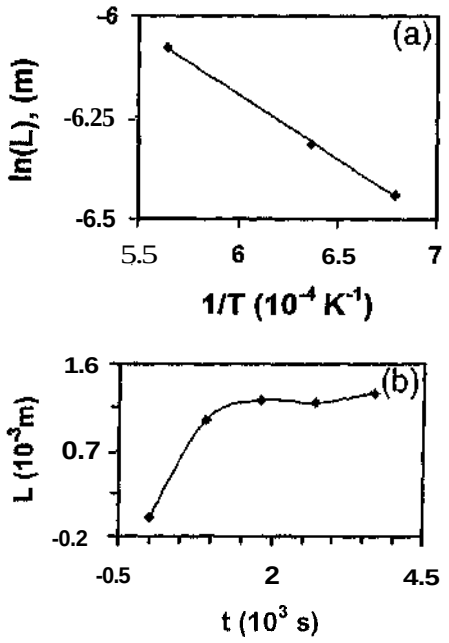


Fig. 5. (a) ln L vs $1/T$ plot with t = 20 min. (b) L vs t plot at 1400°C for the RMI of aluminum into Mo_5Si_3 preform.

at 1400°C and the duration of infiltration was varied. The resulting L vs t plot is shown in Fig. 5(b). The length of infiltration initially increases and saturates for higher duration.

Although a reaction is taking place, the activation energy is very low for the process of infiltration of aluminum into Mo_5Si_3. This means that the infiltration process is mainly governed by the viscous flow of aluminum and that reaction (2) is basically hindering the process. The molybdenum that results after the reaction retards the viscous flow of the aluminum. Hence, the activation energy is 26 kJ/mol, three times greater than the activation energy for the viscous flow of aluminum (8.4 kJ/mol).[8] In the L vs t plot, the initial increase in the rate is due to a decrease in the viscosity of aluminum, but after that the increase in the molybdenum content saturates the infiltration process. Therefore, the presence of Mo_5Si_3 in the $MoSi_2$ preform retards the infiltration process.

IV. Conclusion

RMI of aluminum into $MoSi_2$ -I- Mo and Mo_5Si_3 preforms is studied. Irrespective of initial composition, the final product is always $Mo(Al,Si)_2$. Infiltration of aluminum into Mo_5Si_3 preform results in the formation of $Mo(Al,Si)_2$ containing 25-27 at.% o aluminum, whereas with $MoSi_2$ preform only 14–18 at.% alumi num reacts. Also, initial composition of the preform affects the rat of inl'iltration. The presence of Mo_5Si_3 in the hot-pressed $MoSi_2$ -I Mo slows the inl'iltration process, The lower activation energy fo ihe infiltration process in Mo_5Si_3 preform (- 26 kJ/mol as com pared with 300 kJ/mol for $MoSi_2$ preform) indicates that infiltra tion is governed by the viscous flow of aluminum.

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